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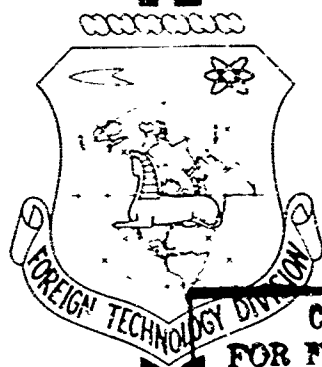VAPORIZATION OF PURE-OXIDE CERAMICS AT HIGH TEMPERATURES

By

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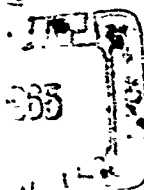## AIR FORCE SYSTEMS COMMAND

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VAPORIZATION OF PURE-OXIDE CERAMICS AT HIGH
TEMPERATURES

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VAPORIZATION OF PURE-OXIDE CERAMICS
AT HIGH TEMPERATURES

Ye. S. Lukin and D. N. Poluboyaninov

(Chemical Technological Institute named after D. I. Mendeleyev)

The use of pure-oxide ceramics at high temperatures in different inert gases and deep vacuum is limited in many cases by the significant vapor pressure of the ceramics, leading to significant weight loss.

The behavior of pure-oxide ceramics at high temperatures can be fully characterized in a calculation of all the parameters affecting vaporization. The most important of these are the nature of the oxides and their purity, the temperature of service, the surrounding gaseous medium and its parameters, the state of the surfaces of samples, their density, peculiarities of structure, etc.

This article is devoted to an investigation of the vaporization of pure-oxide ceramics at different temperatures in a vacuum of 10^{-4} mm Hg and in helium at positive pressure of 0.2 atm. This investigation was conducted to study quantitative vaporization as a technical property so that we could characterize one ceramic in specific conditions of vaporization at high temperatures. In connection with such problems the composition of the products of vaporization were not determined.

A significant number of works are devoted to the study of vaporization of oxides, a determination of the composition of the gaseous phase and the thermodynamic characteristics of the gas-like components. However, the vaporization of ceramics from MgO, BeO, ZrO_2, Al_2O_3 and their compounds $MgO \cdot Al_2O_3$ and $3Al_2O_3 \cdot 2SiO_2$, at high temperatures has been insufficiently studied.

Vaporization was studied on samples of ceramics from pure oxides MgO, Al_2O_3, BeO, CaO, ZrO_3, $MgO \cdot Al_2O_3$, $3Al_2O_3 \cdot 2SiO_2$, which contained about 0.5% impurities. The test samples were prepared according to the technology accepted for the corresponding oxides. The samples had a diameter of 12 – 13 mm, a thickness of 1 – 2 mm, and a weight of 1.0 – 1.5 g. Table 1 gives the characteristics of the samples.

Table 1. Characteristics of Samples of Oxide Ceramics

Oxides[1]	Content of impurities %			
Al_2O_3	0.3	1710	3.82	4.5
BeO	0.3	1950	2.85	5.6
CaO	<1.0	1750	3.05	9.0
MgO	0.3		3.42	4.5
ZrO_2—MgO	0.5		5.35	4.6
ZrO_2—CaO	0.5	1710	5.29	5.5
$MgO \cdot Al_2O_3$	0.5		3.44	3.9
$3Al_2O_3 \cdot 2SiO_2$	0.3		3.04	2.2

[1] ZrO_2 — MgO: specially pure ZrO_2 stabilized by 10 molar % MgO.

ZrO_2 — CaO: specially pure ZrO_2 stabilized by 10 molar % CaO.

The spinel (proposed by I. P. Galkina) is sythesized by sintering from pure magnesium oxide and alumina of brand G-00.

Mullite (proposed by Ye. B. Krol') is preliminarly synthesized from chemically pure Al_2O_3 and SiO_2 of an analytical grade at 1550°C with final sintering at 1710°C.

The impurity content in pure MgO is shown without calculating for the calcium oxide; the quantity of CaO is about 9.7%.

Vaporization was studied at temperatures up to 2300°C in a high-temperature furnace with tungsten heaters. The construction of the furnace and the placement diagram of samples are shown on Fig. 1.

The high-temperature furnace consists of the following basic parts: the body, the upper dome and the heater. The bottom 1, body 2 and cover 9 are equipped with water jackets. Water-cooled copper tubing 3, supported by large copper holders 4, enters the furnace through the bottom. The heater 6, made from molybdenium plates 0.5 – 0.7 mm and tungsten foil 0.2 mm thick, is fastened to the holders by screws. The diameter of the assembled heater is about 20 mm, the height is about 50 – 60 mm. Molybdenum screens 7 are set up around the heater to reduce heat losses. In the center of the heater and screens at one level there is an opening 1.5 – 2 mm in diameter for measuring the temperature of sample 5 by an optical tyrometer, "Pyrolux," with a disappearing thread. It can measure up to 3000°C.

Weight losses during vaporization of ceramic samples were determined on quartz scales of direct weighing. The quartz scales were introduced in the upper dome 10. The samples were suspended on a tungsten or molybdenum wire 8 with a diameter of 0.2 mm. For this the samples had a hole. The length of the wire was 300 – 350 mm. The change in the weight of a sample was determined from the position of the calibrating screw of the quartz coil 11 by a KM-6 cathetometer 12. The accuracy of weighing was 0.0001 g.

During the tests in a vacuum the sample was lowered on the wire to the center of the heater opposite the opening for measuring temperature. When vaporization was determined in helium the sample was lowered into a zirconium dioxide crucible, which prevented the

To the vacuum pump
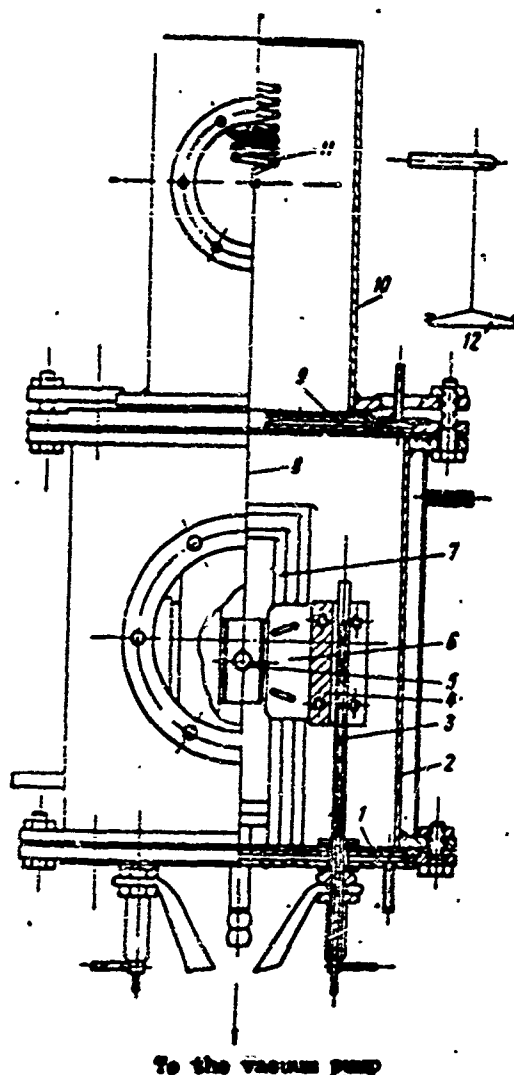
Fig. 1. Diagram of a high-
temperature furnace for
determining weight losses
in a vacuum.

deposition of tungsten from the heater onto it. Also, next to the

hanger we lowered a molybdenum wire 2 — 3 mm in diameter so that the

products of vaporization, rising upwards, would condense not on the

hanger, but on this wire, which had a surface considerably larger

than that of the hanger.

Before and after the tests the samples were weighed on analytical

scales with accuracy up to 0.0001 g. In determining weight loss in

a vacuum we introduced a correction for vaporization of the hanger. It

was determined in a dry run. The divergence in total weight loss

of samples during vaporization, determined by weighing before and

after the tests and by direct weighting with a cathetometer, did not exceed 0.0005 g (0.3%).

As a result of these investigations we determined the dependence of vaporization of oxide ceramics on temperature in a vacuum and in helium (Fig. 2), and also the rate of vaporization at different temperatures. The vaporization of different types of ceramics depends on the nature of the initial oxide. For all oxides we can set the temperature of the start of noticeable vaporization (1 g/cm^2 10^{-3} or ≈ 0.2% by weight). Pure magnesium oxide starts to vaporize at 1700°C; spinel, at 1800°C; Al$_2$O$_3$, at 1900°C; zirconium dioxide stabilized with CaO, at 2000°C; BeO and ZrO$_2$ stabilized with MgO, at 2100 — 2150°C.

Alumina, spinel, zirconium dioxide and beryllium oxide vaporize significantly less than pure magnesium oxide. The vaporization of oxides is significantly less in helium at 0.2 atm than in a vacuum. The temperatures of noticeable vaporization move into a region of higher, more curved dependences of vaporization on temperature with a flatter slope in helium than '.. a vacuum. Such a course of curves can be explained by the difference in the processes in vaporization in helium and in a vacuum. In a vacuum the products of vaporizaion are gradually drawn off during vaporization, which greatly stimulates the removal of molecules from the surface of the sample. In helium the removal of molecules of the material is determined by their diffusion into the gaseous phase, and also by the convection that takes place at high temperatures.
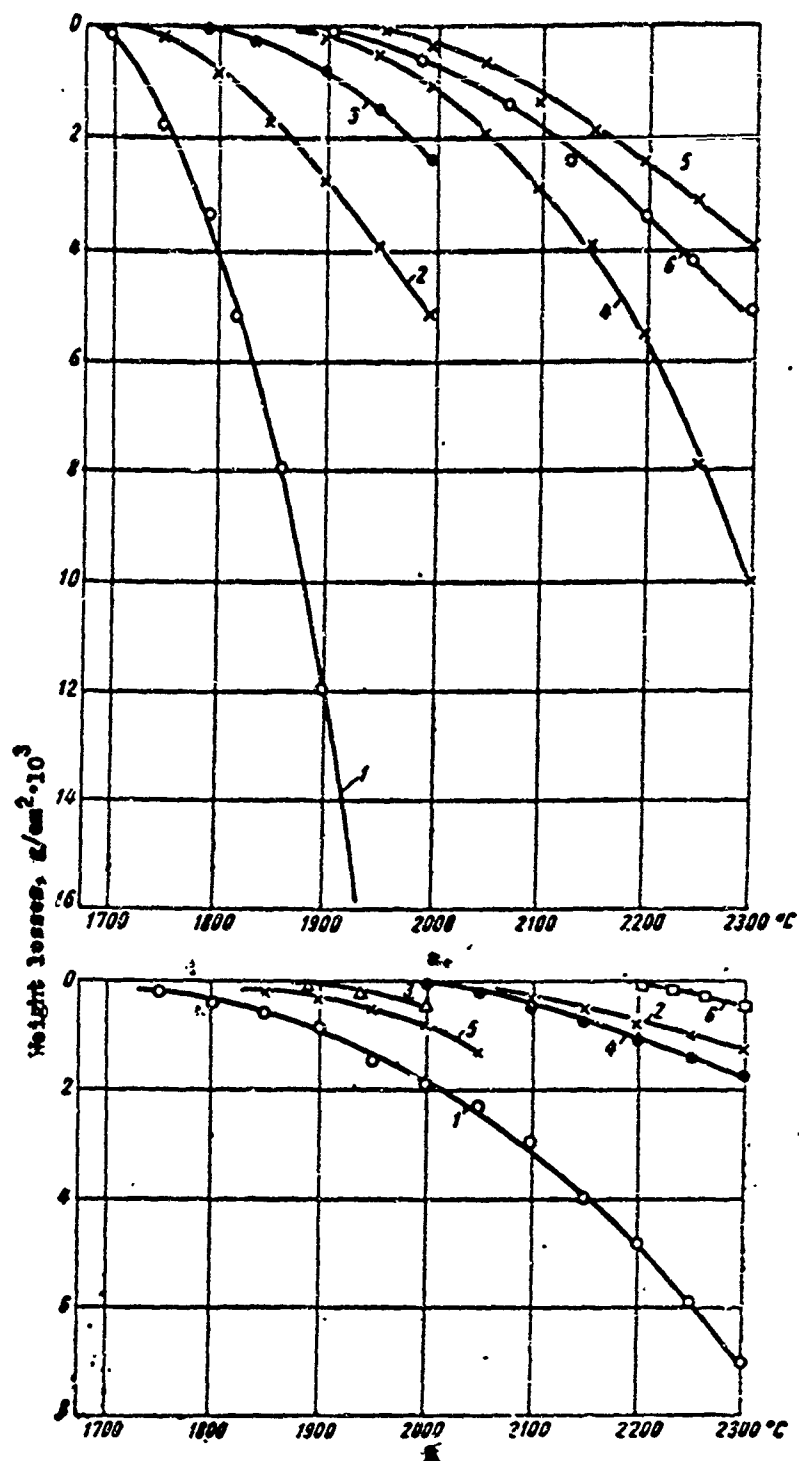
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Fig. 2. Dependence of vaporization of oxide
ceramics on temperature: a) in a vacuum of
10^{-4} mm Hg; b) in helium at 0.2 atm; 1) MgO;
2) $MgO \cdot Al_2O_3$; 3) Al_2O_3; 4) ZrO_2 stabilized by
CaO; 5) ZrO_2 stabilized by MgO; 6) BeO.

For a number of oxides our obtained results fully coincide with the literary data. As a result of a study of the behavior of refractory oxides in a vacuum of 10^{-4} mm Hg, the following temperatures of vaporization were obtained [2]: for ZrO_2, 2300°C; for MgO, 1600°C; for BeO, 2100°C.

A comparison of the magnitudes of vaporization shows that certain oxides are rather stable at high temperatures. Thus, the temperature of noticeable vaporization of MgO in air [2] is 1900°C, BeO, 2400°C, Al_2O , 1750°C, CaO, 1700°C. In the opinion of a number of authors, beryllium oxide is stable up to 2000°C; other investigators [3] claim BeO does not volatilize in a vacuum up to 2200°C. However, in the presence of water vapors BeO vaporizes intensely at 1300 – 1500°C [3]. From the results of our work we conclude that BeO is fully stable in a vacuum of 10^{-4} mm Hg up to 2000°C. Upon heating above 2100 – 2150°C the samples start to vaporize noticeably; at 2200°C about 10% by weight (the weight of a BeO sample was about 1.5 g) vaporizes in 1 hr; at 2300°C in the same conditions approximately 35% by weight vaporizes in 1 hr. In helium vaporization of BeO samples is not observed up to 2200°C; insignificant weight losses occur at 2300°C.

In spite of the stability of beryllium ceramics in helium up to high temperatures, their use in thermal shocks in service at temperatures above 200°C encounters great difficulties. This is because in the interval of 2160 – 2300°C BeO undergoes polymorphous transformation accompanied by an increase in linear dimensions of articles up to 4%. Even small BeO discs and cylinders, heated to 2300°C, are completely destroyed upon sharp cooling. The literature also makes reference to the polymorphous transformation of beryllium oxide [4,7]

The rate of vaporization (Fig. 3) of samples from Al_2O_3, BeO,

ZrO_2 stabilized by MgO and CaO, at 2000°C in a vacuum are within limits of $1 \cdot 10^{-5} - 2 \cdot 10^{-5}$ g/cm²·min. The rate of vaporization of spinel ($MgO \cdot Al_2O_3$) at 2000°C is one order greater, and that of pure magnesium oxide is two orders greater than the stated oxides.
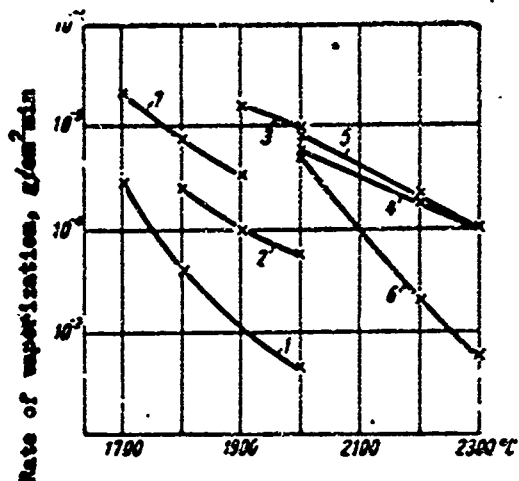
Fig. 3. The rate of vaporization of pure-oxide ceramics in a vacuum depending upon temperature: 1) MgO: 2) $MgO \cdot Al_2O_3$; 3) Al_2O_3; 4) ZrO_2 stabilized with CaO; 5) ZrO_2 stabilized with MgO; 6) BeO; 7) $3Al_2O_3 \cdot 2SiO_2$.

As the temperature is increased the rate of vaporization of all oxides increases, especially strongly for ceramics from MgO and BeO. An increase in the rate of vaporization by two orders (from 10^{-5} to 10^{-3}) is observed for MgO in the interval of 1700 — 2000°C, and for BeO ih the interval of 2000 — 2300°C. The weight losses for MgO samples at 2000°C in a vacuum are about 40%, for BeO samples at 2300°C about 35%.

The rate of vaporization of ZrO_2 stabilized with CaO at temperatures up to 2300 C is somewhat higher than that zirconium dioxide stabilized with MgO. Evidently, this is mostly explained by technological factors. The stabilization of ZrO_2 by introducing calcium oxide proceeds

through the formation of zirconates, which in turn give solid solutions with zirconium dioxide. A determination of the rate of vaporization of calcium zirconate itself shows intensive volitilization somewhat above 1800°C. Also, the radius of the Ca^{2+} ion (1.06) is somewhat larger than the radius of the Zr^{4+} ion (0.87). When a calcium ion is introduced into the ZrO_2 grid some distruction of the structure occurs and the grid constant is increased in comparison with the Mg^{2+} ion (0.78), which evidently can also affect vaporization of zirconium dioxide. We should note that at 2200°C and higher in a vacuum and in helium samples of zirconium dioxide become black with a metallic shine.

The literature [1] states that at high temperatures ZrO_2 is depleated of oxygen and the ratio between O and Z decreases from 2.0 to 1.97 — 1.96, and the free zirconium evidently forms a solid solution with zirconium dioxide. This change in stoichiometry in no way affects the refractory properties of ZrO_2 ceramics. The temperature of the start of defoxmation under load of such a ZrO_2 sample, preliminarily heated in a vacuum to 2300°C, is not different from the temperature of softening of ordinary ceramics from zirconium dioxide. The process of vaporization of stabilized ZrO_2 is rather complex and is evidently connected with joint vaporization of the stabilizer and the zirconium dioxide itself.

The investigation of $3Al_2O_3 \cdot 2SiO_2$ at $1700 - 1900^\circ$C has established a comparatively low rate of vaporization. However, at $1800 - 1900^\circ$C the rate of vaporization of mullite is somewhat higher than that of alumina. The vaporization of mullite is evidently connected with partial disassociation into elements and volitilization of SiO and Al_2O [1, 5]. The rate of vaporization of spinel in a vacuum at all

temperatures is approximately one order less than the rate of vaporization of pure magnesium oxide.

The rate of vaporization of oxide ceramics is less in helium than in a vacuum (Table 2).

Table 2. Rates of Vaporization of Oxide Ceramics in a Vacuum and in Helium at Different Temperatures, $g/cm^2 \cdot min$

Oxides	Temperature, °C					
	2000		2200		2300	
	In vacuum	In helium	In vacuum	In helium	In vacuum	In helium
Al_2O_3	$1 \cdot 10^{-5}$	$0.86 \cdot 10^{-5}$	—	—	—	—
MgO	$2,1 \cdot 10^{-3}$	$2,8 \cdot 10^{-4}$	—	$4,1 \cdot 10^{-4}$	—	$8,25 \cdot 10^{-4}$
BeO	$2,1 \cdot 10^{-5}$	—	$4,7 \cdot 10^{-4}$	—	$1,75 \cdot 10^{-3}$	$1,8 \cdot 10^{-5}$
$MgO \cdot Al_2O_3$	$1,75 \cdot 10^{-4}$	$5,11 \cdot 10^{-5}$	—	—	—	—
ZrO_2—CaO	$1,9 \cdot 10^{-5}$	$1,5 \cdot 10^{-5}$	$5,65 \cdot 10^{-5}$	$4,0 \cdot 10^{-5}$	$9,1 \cdot 10^{-5}$	$5,7 \cdot 10^{-5}$
ZrO_2—MgO	$1,4 \cdot 10^{-5}$	$1,1 \cdot 10^{-5}$	$4,45 \cdot 10^{-5}$	$3,0 \cdot 10^{-5}$	$9,8 \cdot 10^{-5}$	$4,5 \cdot 10^{-5}$

Figure 4 shows the rate of vaporization of MgO and $MgO \cdot Al^2O^3$ depending upon the duration of heating at 2000°C.

The vaporization of ceramics from pure magnesium oxide at 2000°C is a whole order less in helium than in a vacuum. As the temperature is increased the rate of vaporization increases, but significantly less than in a vacuum at the same temperature gradient. The rate of vaporization of spinel at 2000°C is approximately three times less. The rate of vaporization ZrO_2 stabilized with MgO and CaO, as that of BeO, is low even at 2300°C: the weight losses of samples are about 1% in an hour.

During vaporization of MgO and $MgO \cdot Al_2O_3$ ceramics in helium the products of vaporization condense on the cold portions in the form of thread-like crystals of magnesium oxide and spinel.

Thus, in a vacuum and in helium at all temperatures pure magnesium oxide ceramics vaporized most of all. However, in practice in many case for the production of articles we use MgO with additions of alumina, which particularly increases the thermal stability of ceramics.

An investigation of the vaporization of such samples in a
vacuum and in helium at $2000°C$ showed that additions of alumina,
even in comparatively small quantities (4 and 8%), significantly
decreased vaporization. The addition of 4% of alumina in MgO
decreased the rate of vaporization in a vacuum by more than two
times (Table 3). Increasing the quantity of Al_2O_3 to 8% did not
give a significant effect. In helium the rate of vaporization of
samples with additions of Al_2O_3 is 25 – 30% less than that of pure
magnesium oxide. The large difference in the effects of additions
on vaporization in helium and in a vacuum is evidently explained by
the character of prossesses of vaporization of magnesium oxide in
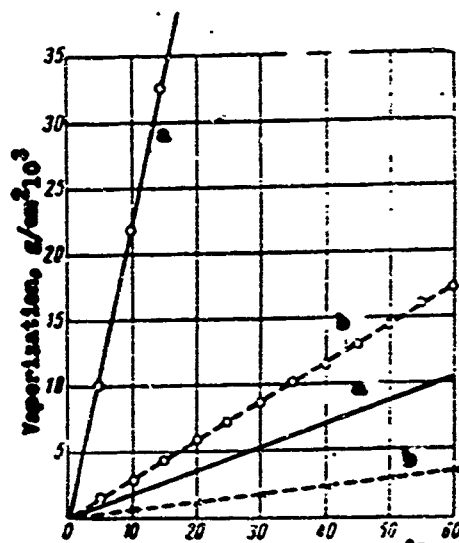these conditions.

Fig. 4. Rate of vaporization:
a) in a vacuum; b) in helium;
1) MgO; 2) MgO·Al_2O_3

Table 3. Rate of Vaporization of Ceramics from Magnesium Oxide with Additions of Al$_2$O$_3$ at 2000°C

Oxides			Rate of vaporization, g/cm^2·min	
			In a vacuum	In helium
MgO	3.42	4.5	$2.1 \cdot 10^{-3}$	$2.8 \cdot 10^{-4}$
MgO+ +4% Al$_2$O$_3$	3.44	3.9	$8.2 \cdot 10^{-4}$	$2.1 \cdot 10^{-4}$
MgO+ +8% Al$_2$O$_3$	3.45	3.7	$7.4 \cdot 10^{-4}$	$1.9 \cdot 10^{-4}$
MgO·Al$_2$O$_3$	3.44	3.9	$1.75 \cdot 10^{-4}$	$5.11 \cdot 10^{-5}$

Specific gravity and porosity change in the process of vaporization of samples of certain oxides (Table 4). Of all the tested oxides open porosity was revealed after tests at high temperatures only in samples of MgO and BeO. This indicates that vaporization in a vacuum occurs not only from the surface, as in helium, but additionally from within the sample. The specific gravity of samples of other oxides increased somewhat, which is evidently connected with some additional sintering at higher temperatures than during their first kilning. In helium closed porosity was retained by all samples and their specific gravity increased somewhat. Samples of MgO and MgO·Al$_2$O$_3$ were glazed after tests in helium.

Table 4. Specific Gravity and Porosity of Pure-Oxide Ceramics after Tests

Oxides	Temperature	Test conditions		Specific gravity, g/cm^3		Apparent porosity after testing
				Before testing	After testing	
Al$_2$O$_3$	2000	In a vacuum		3.82	3.87	0
BeO	2200	»	»	2.85	2.62	7.9
ZrO$_2$—MgO	2000	»	»	5.35	5.36	0
ZrO$_2$—CaO	2300	»	»	5.28	5.52	0
MgO·Al$_2$O$_3$	2000	»	»	3.44	3.41	0 85
MgO	1800	»	»	3.42	3.39	2.93
MgO	2000	»	»	3.42	3.12	12.7
MgO	2200	In helium		3.42	3.49	0
BeO	2200	»	»	2.85	2.90	0

Preliminary investigations of the vaporization of ceramics from oxides with total porosity of 50 — 70% have shown that samples from Al_2O_3, ZrO_2, BeO and MgO, prepared by burning out additions and by the foam method, vaporized in a vacuum approximately 1.5 — 2 times more by weight than dense samples of the corresponding oxides.

In our investigation of vaporization we weighed the samples on a tungsten or molybdenum wire 0.2 mm in diameter, which allowed us to establish the character of their interaction at high temperatures. In a vacuum and in helium we observed no interaction on the contact of the hanger from W and Mo with samples of Al_2O_3, $MgO \cdot Al_2O_3$ up to 2000°C, from mullite up to 1900°C, from BeO and specially pure, stabilized ZrO_2 up to 2300°C. Interaction of tungsten and molybdenum with magnesium oxide was noted at temperatures above 1800°C, when its intenses vaporizations started. The greatest interaction of W and Mo occured with calcium oxide. In connection with this we should note the peculiarity of the behavior of CaO in a vacuum and in helium at high temperatures. Calcium oxide evidently obsorbes the tungsten vaporized from the heater from the gaseous phase very intensely. In a vacuum a sample increased in weight by approximately 2% from 1200 to 2000°C. At 2000°C a sample usually breaks due to the very intensive reaction at the contact with a W or Mo hanger. All CaO samples became black after testing. The measures taken to protect the sample from deposition of tungsten did not give a positive result. The same thing also occured in helium.

The applied method investigation is esentially the method of vaporization from an open surface in a Langmuir vacuum. Proceeding from this and knowing the products of a gaseous phase, from the rate of vaporization we can calculate the vapor pressure of the

corresponding materials according to the formula [6]:

$$G = \alpha P \sqrt{\frac{M}{2\pi RT}}.$$

where G is the rate of vaporization, g/cm$^2 \cdot$ sec; P is the vapor pressure, dyne/cm^2; α is the coefficient of accomidation; M is the molecular weight of the vapor; R is the gas constant, erg/deg$\cdot$mole; T is the absolute temperature, $^\bullet$K.

In our investigation we did not determine the composition of the gaseous phase during vaporization; the literature contains very contradictory data about its composition above the vaporizing oxides at high temperatures. Therefore, in most cases it was not possible to calculate vapor pressure and compare it with the literary data without determining the composition of the gaseous phase in the specific conditions of our task. Let us give the results of calculating the vapor pressure of BeO during vaporization of beryllium ceramics according to our tests at 2000$^\bullet$C proceeding from the assumption that molecules of beryllium oxide are vaporizing:

Source	Temperature, $^\circ$C	Vapor pressure
Our tests	2000	$8.15 \cdot 10^{-9}$
[3]	2000	$8.30 \cdot 10^{-9}$
[3]	1969	$7.50 \cdot 10^{-9}$

Conclusions

The developed method of investigating vaporization allowed us to study the behavior of widely applied oxide ceramics at temperatures up to 2300°C in a vacuum and in helium.

At such temperatures all oxides vaporize, but in different manners depending upon their nature and the test conditions. One should look for the causes of the different vaporization of oxides

in the crystalline structure of the substance itself, because
vaporization depends on the type of crystalline grid and its energy
and, consequently, is determined by the strength of the bond between
atoms or ions of the substance.

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